ON THE TENDENCY OF AIR AND THE DIFFERENT GASES TO MUTUAL PENETRATION:

A PROBATIONARY ESSAY,

SUBMITTED TO

THE FACULTY

OF

PHYSICIANS AND SURGEONS OF GLASGOW.

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ESSAY.

On the tendency of Air and the different Gases to Mutual Penetration.

WHEN a light and heavy gas are mixed together, they do not exhibit any tendency to separate again from each other, on standing at rest for a length of time, differing in this respect from mixed liquids, which speedily separate from each other, and arrange themselves according to their density, the lightest uppermost and the heaviest undermost, as in the familiar example of oil and water, unless they have combined together. This peculiar property of gases has repeatedly been made the subject of careful experiment. Common air, for instance, is essentially a mixture of two gases, differing in weight in the proportion of 0.972 to 1.111, but the air in a tall close tube of glass several feet in length, kept upright in a still place, has been found sensibly the same in composition at the top and bottom of the receiver, after a lapse of months. Hence there is no reason to imagine that the upper strata of the air differ in composition from the lower, with which we are acquainted; or that a light gas, such as hydro-

gen, escaping into the atmosphere, will rise and ultimately possess the higher regions, suppositions which philosophers have made the groundwork of meteorological theories at different times.

Mr. Dalton, at an early period in his philosophical career, perceived the important bearings of this property of aërial bodies, involving as it does the doctrine of evaporation and the retention of vapour in the atmosphere, and made it the subject of experimental inquiry. He made the discovery that any two gases, allowed to communicate with each other, exhibit a positive tendency to mix or to penetrate through each other, even in opposition to the sedative influence of their weight. Thus a vessel containing a light gas, being placed above a vessel containing a heavy gas, and the two gases allowed to communicate by a narrow tube, an interchange speedily took place of a portion of their contents, which it was natural to suppose that their relative position would have prevented. Contrary to the solicitation of gravity, the heavy gas continued spontaneously to ascend and the light gas to descend, till in a few hours they became perfectly mixed, and the proportion of the two gases was the same in the upper and lower vessels. This disposition of different gases to intermix, appeared to Mr. Dalton so decided and strong, as to justify the inference that gases afford no resistance to each other; but that one gas spreads or expands into the space occupied by another gas, as it would rush into a vacuum. At least, that the resistance which the particles of one gas offer to those of another is of a very imperfect kind, to be compared to the resistance which stones in the

channel of a stream oppose to the flow of running water. Such is Mr. Dalton's theory of the miscibility of the gases. Vapours from volatile liquids rise into air from the same cause.

M. Berthollet afterwards conducted a series of experiments of the same nature in the most favourable circumstances, in the caverns under the observatory of Paris, where the air is undisturbed, and the temperature constant. But although the careful experiments of the last philosopher, place the fact of the spontaneous diffusion of gases beyond a doubt, yet they elicit nothing new, except perhaps the circumstance that hydrogen is more penetrating and diffusive than any of the other gases. Berthollet did not adopt the mechanical theory of Dalton to account for this tendency of gases to intermix; but supposed that it was the effect of a chemical attraction for each other subsisting between the particles of different gases.

Some chemical writers, however, have been disposed to overlook both the chemical theory of Berthollet, and the mechanical explanation of Dalton, and to view the intermixture of gases communicating with each other, as sufficiently accounted for by the action of external disturbing causes operating upon their elasticity and extreme mobility.

Upon entering on this inquiry, I very soon found that the last supposition is altogether inadmissible, and that the diffusion of gases is not of an accidental nature, but subject to fixed laws, which equally apply to the elevation of Vapours into air and the permanent gases. Some of my researches on this subject have already been given to the world, (Quarterly Journal

of Science, New Series, vol. V.) The principal results contained in that publication, I shall shortly state, and then proceed to give an account of some more recent investigations into the same subject.

1. Gases diffuse into the atmosphere, and into each other, with different degrees of ease and rapidity. This was determined by allowing each gas, to diffuse from a receiver into the air, through a narrow tube, taking care that when the gas was lighter than air, it was allowed to escape from the lower part of the vessel, and when heavier from the upper part, so that it had on no occasion any disposition to flow out, but was constrained to diffuse in opposition to the solicitation of gravity.

In the first set of experiments, after diffusion for ten hours, the receiver containing at the outset 150 measures of gas, there remained,

Gases.	Sp. gr. Air=1.	Measures left in the receiver.	Escaped into the atmosphere.
Hydrogen	0.0694	8.3	141.7
Carbureted hydr.	0.5555	56.	94.
Ammoniacal	0.59027	61.	89.
Olefiant	0.97220	77.5	72.5
Carbonic acid	1.5277	79.5	71.5
Sulphurous acid	2.2222	81.	69.
Chlorine	2.5	91.	59.

After four hours, out of 152 measures,

Gases.	Left in the receiver.	Escaped.
Hydrogen,	28.1	123.9
Carbureted hydrogen,	86.	66.
Ammoniacal,	89.	63.
Olefiant,	99.	53.
Carbonic acid,	104.	48.
Sulphurous acid,	110.	42.
Chlorine,	116.	36.

If we attempt to deduce from the foregoing Tables the comparative diffusibilities of different gases, it will be necessary to keep in mind, that the rate at which the latter portions of gas leave the receiver is a diminishing one. In the case of olefiant gas, it was determined with precision, that the gas continues to leave a receiver by diffusion, according to the same diminishing rate which holds in mechanical exhaustion by the air-pump. Hence the initial diffusions of the gases are even more varied than the numbers in the Table. As much hydrogen gas left a receiver in two hours, as of carbonic acid in ten hours; hence the former gas is five times more diffusible than the latter. Nor was the rate of diffusion that which might have been expected from differences of sp. gr.; for carbureted hydrogen and ammoniacal gas left the receiver in greater proportions than olefiant gas, although the diffusion of the two former was more opposed by mechanical means. It is evident that the diffusiveness of the gases is inversely as some function of their density—apparently the square root of their density.

The effect of the position of the receiver was shown by an experiment on hydrogen gas. Other circumstances being the same as in experiment Table 1, (where only 8.3 parts of hydrogen gas out of 150 were left after ten hours,) 22.1 parts were found remaining in the receiver, its position during that interval having been vertical, instead of horizontal.

2. My next object was to determine, whether, when an intimate mixture of two gases is left in the receiver, each gas leaves the receiver independently of the

other, in the proportion of its individual diffusiveness. For this purpose, the receiver was entirely filled with an intimate mixture of different gases in various known proportions to each other. For instance, equal volumes of hydrogen and olefiant gases (150 vols. in all) being left together ten hours, the following results were obtained:

	Found in the receiver.	Escaped.
Hydrogen gas	3.5	71.5
Olefiant gas	56.6	18.4
Air	89.9	
	150.	150.

The most diffusive gas had therefore separated from the other, and left the receiver in the greatest proportion. On comparing these results with those of the foregoing Tables, it will be seen that the disparity between the diffusiveness of each of the gases, taken in a state of mixture, is actually greater than the disparity between the diffusiveness of the same gases taken separately. In the case of mixed gases, the law, as deduced from upwards of forty experiments on different mixtures, is—that the more diffusive gas leaves the receiver in a *greater* proportion than in the case of the solitary diffusion of the same gas: and the less diffusive gas in any mixture, in a *less* proportion than in its solitary diffusion.

By availing ourselves of these tendencies in mixed gases to diffuse in different degrees, a sort of mechanical analysis of mixed gases may be carried on. Suppose, for example, we had a mixture in equal volumes of two gases, of the same densities as carbonic

acid and carbureted hydrogen, not separable from each other by chemical means: allow this mixture to diffuse for a certain time, into a gaseous or vaporous atmosphere, of such a kind as may afterwards be absorbed or condensed with facility. On condensing the latter atmosphere, there would remain a mixture consisting of one part of the light and one of the heavy gas. Continue these operations in a series, and the proportion of the light gas will progressively increase. If a specimen of the dense gas be required, a converse series of operations must be pursued.

3. The diffusion of gases into other atmospheres besides common air was also examined. A phial, containing 5.2 cubic inches, provided with a perforated cork, was filled with an intimate mixture of olefiant and hydrogen gases in equal proportions: and was connected, by a tube and another perforated cork, with a second bottle of the capacity of 37 cubic inches, containing carbonic acid gas. The phial had the highest station; and to prevent contact with the external air, the apparatus was sunk in water below the joinings. After ten hours, the phial was found to contain, independently of carbonic acid, olefiant and hydrogen gases in the proportion of 12 to 3.1. In this case, the olefiant gas would undoubtedly have been obtained purer, had the original mixture been allowed to diffuse *upwards*, and into an atmosphere of specific gravity intermediate between that of its constituent gases—into steam or ammoniacal gas, for instance, for then circumstances would have been most conducive to the unequal diffusion and separation of the mixed gases.

The tendency to diffusion among gases being inversely as their densities, the lighter gases are more rapidly penetrated by any given vapour than the heavier ones. Hydrogen gas is expanded, for instance, by ether, four times more rapidly than atmospheric air. Consistently with the same principle, the heaviest vapours are by much the most slowly diffused; that of alcohol, for example, spreads more slowly through any gas than aqueous vapour. Expansion by heat increases the diffusive property; and in this way, the increased facility with which gases, at a red heat, penetrate in both directions through porcelain tubes, may be accounted for, and not from increased diameter of the pores of the porcelain.

It is evident, therefore, that the diffusion of a gas into air, does not take place in sensible masses, but in ultimate particles; otherwise mixed gases could not diffuse unequally.

That the unequal diffusion is the result of any attraction between the gases and the surface of the narrow glass tube by which they escape, is by no means likely. For the same separation took place in a curious experiment, in which the interference of such an attraction cannot be supposed. A receiver 3-4ths of an inch in diameter, and several inches in height, standing over water, contained a mixture of 2 hydrogen, and 1 oxygen, with which it was not entirely filled. A little sulphuric ether being thrown up, caused the gas to expand with rapidity, so that the receiver became full, and a portion of the gas was projected. This portion, which had diffused downwards with greatest rapidity to meet the ether vapour, had its proportion of hydrogen

doubled, so that a separation had been effected by the agency of diffusion alone.

The preceding experiments discountenance any theory, such as that of Berthollet, which supposes the diffusion to be induced by a chemical attraction between the particles of different gases. For it is extremely unlikely that the intensity of that attraction, and the consequent rapidity of the diffusion, should depend entirely on the density of the gas, as we have found to be the case. The experiments appear compatible, however, with the mechanical theory of Dalton.

On Dalton's theory, gases should mutually press through each other, with a force equal to that of the pressure of the atmosphere—they are passing into vacua. Vapours from liquids on the verge of their boiling temperature, rise and penetrate through air with such a force, as is easily proved by the doubled tension of a portion of air confined over a liquid in these circumstances. But we have not the same means of ascertaining the force with which two gases penetrate each other. Their bulk and tension must continue the same, although they should penetrate each other with a force equivalent to the pressure of the atmosphere. At first sight, there appears to be no evident method of ascertaining the amount of this force. But that different gases communicating with each other, do diffuse with a substantial force, and that that force is equal to the pressure of the atmosphere, I believe I shall be able to render probable, by a curious series of experiments.

There is a singular observation of Dœbereiner, which chemists seem to have neglected as wholly inexplicable, on the escape of hydrogen gas by a fissure

or crack in glass receivers, from which I set out in this inquiry. Having occasion while engaged in his researches on spongy platinum, to collect large quantities of hydrogen gas, he had accidentally made use of a jar which had a slight crack or fissure in it. He was surprised to find that the water of the pneumatic trough rose into this jar $1\frac{1}{2}$ inches in 12 hours; and that after 24 hours, the height of the water was 2 inches two-thirds. During the experiment neither the height of the barometer, nor the temperature of the place had sensibly altered.

In other experiments, he substituted glass vessels of very different forms, tubes, bell-jars, flasks, all of which had fissures. In every one of these vessels filled with hydrogen, the water rose, after some hours, to a certain height. On covering one of these vessels containing hydrogen, by a receiver; or on filling the vessel with atmospheric air, oxygen, or azote, instead of hydrogen, he never observed a change in the original volume of the gas. He thinks it probable that the phenomenon is due to the capillary action of the fissure, and that hydrogen only is attracted by the fissures, and escapes through them on account of the extreme smallness of its atoms.

This explanation is rendered improbable by the circumstance, that hydrogen, of all the gases, was found to be condensed and absorbed with greatest difficulty and in smallest quantity, by charcoal and the other porous substances tried by Saussure. And we have no reason to suppose that the particles of hydrogen are smaller than those of the other gases.

On repeating the experiment of Dœbereiner, and

varying the circumstances, it appeared that hydrogen never escapes outwards by the fissure without a certain proportion of air returning inwards. Now on Dalton's theory, the external atmosphere is a vacuum to the hydrogen, to which the latter has access by the small fissure, while the jar of hydrogen is a vacuum to the external air. The hydrogen and air should therefore mutually diffuse into each other. But we know that hydrogen is three or four times more diffusive than air; and an effect of this seems to be, that three or four volumes of hydrogen leave the receiver by the fissure, through the operation of diffusion, for every single volume of air which enters it. Consequently the bulk of gas in the receiver is diminished, and the water rises in it. This appears to me to be the true explanation of the phenomenon; and it promises the opportunity we are in search of, of making an estimate of the force with which gases spontaneously penetrate through each other. It is necessary that the fissure be extremely small, and all my attempts to make an artificial fissure to answer this purpose have failed.

In Dœbereiner's experiment, as soon as the water rises in the jar above its outer level, air will begin to be forced into it mechanically, independently of what enters by diffusion. But if we press down the jar of hydrogen to a certain depth in the water trough, so that the level of the water without is kept constantly higher than the level of the water within the jar; then, besides the hydrogen which leaves the jar by diffusion through the fissure, a portion will be forced out mechanically by the pressure to which it is subject. In the last circumstances, however, no air can enter by

the fissure and mix with the hydrogen, except by diffusion. Now in upwards of a dozen experiments of this kind, the air which entered by diffusion amounted to between 1-5th and 1-4th of the hydrogen, which left the receiver at the same time. But when the circumstances were reversed and the column of water allowed to rise in the jar, the quantity of air which entered by diffusion was increased by a portion which entered mechanically; and varied from a third to a fourth part of the quantity of hydrogen which escaped by the fissure.

In one experiment, for example, in which the water rose in the jar 0.7 inch above the level in nineteen hours—instead of 48 cubic inches hydrogen there were found

38.7	Hydrogen.
3.3	Air.
6.0	Loss.
48.0	

Here 6.0+3.3, or 9.3 cubic inches hydrogen have left the receiver by the fissure, while 3.3 air have entered. The hydrogen which has escaped, has been replaced by fully more than a third of its bulk of air.

In another experiment, a jar with a fissure was filled with hydrogen and pressed down by weights in the water trough, so that the water without was at first 3.2 inches above the level of the water within the jar. In four days, the water within the jar had approached to 0.4 inch of its height without. Instead of the original 27 inches of hydrogen, there was now found to be

9.55 Hydrogen.
3.25 Air.
14.20 Loss.

27.00

In this experiment for 17.45 inches hydrogen, which have left the receiver, 3.25 air have at the same time entered by diffusion, although the ingress of the latter, at the beginning of the experiment, was opposed by the pressure of a column of 3.2 inches water, and even at the last by a column of 0.4 inch. The air does not amount to 1-5th part of the hydrogen which has escaped, a portion of the last having undoubtedly been forced out mechanically.

When hydrogen is kept over water for any length of time, it is known that a little air rises into it from the water, which might be suspected in the preceding experiments. But hydrogen confined in a sound jar over water, was found to acquire only 0.8 per cent. air in four days, and 2 per cent. in a month; so that the air found in the jar in the last experiment, and in many others of the same kind, must have entered by the fissure, and by the agency of diffusion.

The air which entered by diffusion in these cases, was identical in composition with the external atmosphere.

When a mixture of hydrogen and olefiant gas was retained in a jar with a fissure, it was the hydrogen principally which left the receiver, while the most of the olefiant gas remained, as might be expected from the relative diffusiveness of these two gases.

In a jar with a fissure entirely filled with coal gas, or with carbureted hydrogen of marshes, and standing

over water, a slight but perceptible contraction always took place, due to the circumstance that these light gases, like hydrogen, are not replaced by so much as an equal bulk of air, on diffusing through the fissure.

With olefiant gas and carbonic oxide, which approach to the density of air, no contraction was perceptible, not attributable to other causes.

In the case of carbonic acid, a slight but positive expansion appeared to take place in the bulk of the contents of the jar, the experiment being performed over mercury.

It appears then that the gas introduced into the jar with a fissure, whatever it may be, leaves the jar, while air enters, in quantities which are proportional to the relative diffusiveness of the gas and of air. If the gas is more diffusive than air, more of it leaves the jar than air enters, and a contraction ensues in the bulk of the gas, as in Dœbereiner's original experiment. The gas and air may be viewed as diffusing through the fissure in opposite directions, quite independently of each other, and with the force peculiar to each. That they are impelled through the fissure with a certain force is evident, for the fissure is so minute that we cannot cause either air, or the gas employed, to flow through it mechanically at the same rate, without the application of considerable pressure.

But there are difficulties in the way of deducing an estimate of the amount of the force with which gases penetrate each other, from experiments of this kind. The fissure or opening never allows diffusion to go on at the same rate in two successive experiments, principally, I believe, from its size changing with variations in its state in regard to humidity.

The effects were made much more striking, in some respects, by the discovery that Wedgewood stoneware tubes, such as are used in furnace experiments, admit, from their porous structure, of being substituted instead of jars with fissures. When shut at one end, as they are sometimes made, they may be managed like other cylindrical gas receivers. Those which are unglazed are most suitable, but do not answer the purpose, if either very dry or too damp, being permeable by a gas under the slightest pressure in the one case, and perfectly air tight in the other.

A cylindrical receiver of this description, 12 inches in depth, and 5.7 cubic inches in capacity, was filled with hydrogen gas over water in the usual way. After 15 hours, it was found to contain 2.35, instead of 5.7 cubic inches of gas, which was principally common air. The water had risen, on this occasion, to the height of 7.1 inches in the receiver.

The diffusion takes place with great rapidity. The stoneware cylinder was filled with hydrogen over water, and transferred to the mercurial trough: in 40 minutes, the mercury had risen to the height of $2\frac{1}{2}$ inches in the receiver, and it was found to contain in 100 parts,

51.9	Hydrogen.
24.4	Air.
23.7	Loss.
100.0	

Again, the stoneware cylinder was filled with hydrogen as before, transferred to the mercurial trough, and *pressed down* to a depth of four inches in the mercury,

in which situation it was kept for 30 minutes. From 5.7, it was reduced in that time to 4.58 cubic inches. Supposing it to have originally contained 100 parts, they are accounted for thus,

70.7	Hydrogen remaining.
9.6	Air which has entered.
19.7	Loss.
100.0	

Here we find air entering the receiver by diffusion, against the outward pressure of a column of four inches mercury; and nearly as abundantly as in the preceding experiment; for in both cases, about 1 volume of air has entered, and 3 volumes of hydrogen have left the receiver.

The force with which air and hydrogen penetrate each other must be very considerable, since it is not materially affected by a difference equivalent to the pressure of a column of $6\frac{1}{2}$ inches mercury.

The other gases were found to diffuse from the stoneware cylinder, as they did in the case of the glass receiver with fissure.

I was at great pains to determine that the fragments of these stoneware tubes, either wet or dry, possess no capacity to absorb and condense hydrogen gas in their pores, that can be appreciated. So that no fallacy in the experiments need be apprehended from that cause.

FINIS.